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TTF-$NHCO_2(CH_2)_2O$-TCNQBr AND TTF-$CO_2(CH_2)_2O$-TCNQBr, TWO POTENTIAL MOLECULAR RECTIFIERS*

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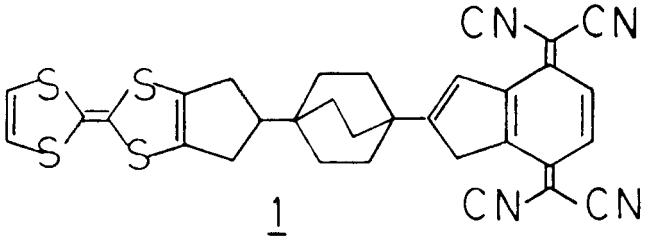
Abstract Aviram and Ratner have proposed that a molecule D-σ-A composed of a good electron donor (D) portion like tetrathiafulvalene, a good covalent electron acceptor (A) similar to 7,7,8,8-tetracyanoquinodimethan, and an insulating bridge of sigma bonds between them, would act as a unidirectional electrical conductor, suitable for use in rectifying devices. We report here the synthesis of two monomeric examples similar to that proposed molecule.

INTRODUCTION

Several years ago, Aviram, Ratner, et al.[1-3] proposed that a molecule of the general type D-σ-A such as 1, composed a good π-electron donor (D) like tetrathiafulvalene (TTF, 2a), a good π-electron acceptor (A) similar to 7,7,8,8-tetracyanoquinodimethan (TCNQ, 3a), and an insulating bridge (σ) of sigma bonds between them, would act as a unidirectional electrical conductor. This may occur because the electronic states D-σ-A and D^+-σ-A^- would be interconvertible under the most moderate electrical bias, but the state D^--σ-A^+ would be energetically inaccessible, assuming that the donor and acceptor properties are only mildly perturbed by the presence of the sigma bridge.

We report the synthesis of the first monomeric examples of the proposed molecule, in which the sigma bridge between the donor and acceptor portions are the ethoxycarbamate, or the ethoxycarboxylate moieties: 2-(5'-



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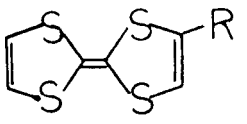
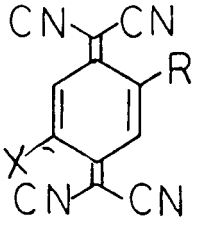
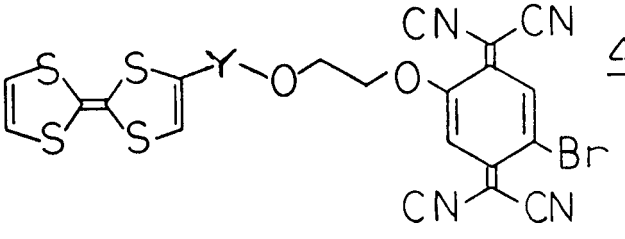


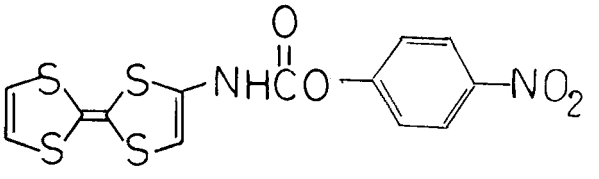
2a R=H
2b R=NCO
2c R=COCl
2d R=CO_2H



3a R, X=H
3b R=OCH_2CH_2OH
X=Br



4 Y=NHC(=O)
5 Y=C(=O)



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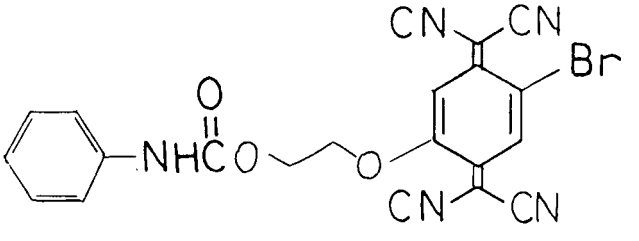

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Bromo-7',7',8',8'-tetracyanoquinodimethan-2'-oxy)ethyl tetrathiafulvalenylcarbamate (4) and its carboxylate analog (5). The molecules 4 and 5 were obtained from the condensation of the known 2-(2-hydroxyethoxy)-5-bromo-7,7,8,8-tetracyanoquinodimethan (3b)[6] with 2-isocyanatotetrathiafulvalene (2b) and 2-chlorocarbonyl-tetrathiafulvalene (2c), respectively. Both intermediates 2b and 2c were prepared from the known 2-carboxytetrathiafulvalene (2d). The former compound (4) has been reported previously elsewhere in preliminary communications.[4,5]

SYNTHESIS

2-(2-Hydroxyethoxy)-5-bromo-7,7,8,8-tetracyanoquinodimethan (3b)

The 7-step synthesis used by Hertler[6] to prepare 3b from 2,5-dimethylphenol was followed, with some modifications, to afford the quinodimethan in a 13% overall isolated yield. Compound 3b crystallized from CH_3CN as dark red needles: mp 220-225°C dec. (lit[6] mp 213-217°C dec.); IR (KBr or CH_3CN) 2200 cm^{-1} (sharp peak)[7]; UV(CH_3CN) 482nm($\log_{10}\varepsilon$ 3.65), 412(4.62), 390(3.60).

Anal. Calcd. for $C_{14}H_7BrN_4O_2$: C, 49.00; H, 2.06; Br, 23.28; N, 16.33. Found: C, 48.80; H, 2.09; Br, 23.72; N, 16.29.

2-Chlorocarbonyltetrathiafulvalene (2c)

2-Carboxytetrathiafulvalene (2d) was prepared[8] from commercially[9] available tetrathiafulvalene. A solution of 0.4 mmol of 2d in 10 mL of dry C_6H_6, 2 mL of dry CH_3CN, and 5 μL of DMF was stirred under argon while 0.64 mmol of distilled oxalyl chloride was added in one portion. After stirring at 25°C for 40 min, the solvents were removed

under reduced pressure. The residue was triturated with dry C_6H_6 and then filtered. The filtrate, after evaporation, afforded the acid chloride of 2d which was recrystallized from hexane to afford dark purple needles (85-90%): mp 130-135°C dec.; IR (KBr) 3080, 1700, 1525 cm^{-1}; NMR ($CDCl_3$) σ 7.72 (s, 1H), 6.31 (s, 2H).

2-Isocyanototetrathiafulvalene (2b)

A solution of 0.37 mmol of the acid chloride, 2c, in 8 mL of anh. CH_3CN was mixed with 0.45 mmol of activated[10] NaN_3 at rm. temp. After 75 min, the red solution was concentrated under reduced pressure without heating. The residue was triturated in a small amount of dry C_6H_6 to afford maroon needles of the acylazide of 2d (88%): mp 108-9°C; IR (CH_3CN) 2150, 1660 cm^{-1}. This was then heated to the reflux temperature in C_6H_6 for 1.5 h. The solvent was evaporated and the residue was recrystallized from C_6H_6-C_6H_{14} in an inert atmosphere to give 2b in 80-85% yield: mp 75-8°C; IR (C_6H_6) 2250 cm^{-1}.

p-Nitrobenzyltetrathiafulvalenylcarbamate (6)

A warm C_6H_6 solution of 2b under Ar was treated with an equivalent amount of p-nitrobenzyl alcohol, followed by a catalytic quantity of dibutyltin dilaurate, and the resultant mixture was heated to 75°C for 30 min and stored at rm. temp. for 16 h. Dark red-purple crystals of p-nitrobenzyl tetrathiafulvalenylcarbamate (6) were collected, washed with cold C_6H_{14} and recrystallized from C_6H_6-C_6H_{14} to afford 6 in 86% yield: mp 154-5°C; IR (KBr) 3340, 3080, 1735, 1600, 1510 cm^{-1}; UV (CH_3CN) 371 nm ($\log_{10}\varepsilon$ 3.67), 350 (3.74), 310 (4.17), 272 (4.31).

Anal. Calcd. for $C_{14}H_{10}N_2O_4S_4$: C, 42.20; N, 7.03; S, 32.18. Found: C, 42.32; N, 6.94; S, 32.29.

2-(5'-Bromo-7',7',8',8'-tetracyanoquinodimethan-2'-oxy)ethyl phenylcarbamate (7)

This urethane was prepared from 3b and phenylisocyanate, and crystallized as deep red needles ($CHCl_3$-C_6H_{14} or CH_3CN) in 81% yield: mp 198-200°C dec.; IR KBr 3380, 3080, 2200 (sharp)[7], 1740-1725, 1595 cm^{-1}; MS: M/e 462.3 (M^+).

Anal. Calcd. for $C_{21}H_{12}BrN_5O_3$: C, 54.56; N, 15.15. Found: C, 54.85; N, 15.32.

2-(5'-Bromo-7',7',8',8'-tetracyanoquinodimethan-2'-oxy)ethyl tetrathiafulvalenylcarbamate (4)

The urethane 4 was synthesized by combining 0.04 M CH_3CN solutions of 2b and 3b (5 mL each) under Ar followed by the addition of 0.1 μL of dibutyltin dilaurate. The red solution was stirred 16 h, during which time it changed to a brown suspension. The solvent was removed to leave 115 mg of a dark brown powder. This was stirred in n-hexane under Ar and filtered after a short period. The hexane filtrate did not yield any residue after evaporation. The filter cake was similarly treated with freshly distilled $CHCl_3$. About 5-10% was soluble and was recovered from the filtrate as a brown solid (minor product 4A): mp 105-108°C: IR (CH_3CN) 3500-3400, 2210 (sharp)[7], 1735, 1600, 1525, 745 cm^{-1}; UV(CH_3CN) 853 nm ($\log_{10}\varepsilon$ 3.40), 752 (3.27), 482 (3.67), 412 (4.54), 401 (4.52), 291 (4.08). The filter cake from the $CHCl_3$ treatment was then washed with CH_2Cl_2 and CH_3CN, consecutively. The two filtrates were combined (they were identical according to TLC, 40% CH_3CN: 60% $CHCl_3$) and the solvents were removed to yield a brownish-purple solid (40-50%) (major product 4B): mp 145-150°C dec.; IR (KBr) 3500-3400, 3080, 2180 (broad)[7], 1740-1700, 1600, 1240-1220 cm^{-1}; UV(CH_3CN) 853 nm ($\log_{10}\varepsilon$ 4.57), 763 (4.24), 690 (2.82),

443 (shoulder, 4.45), 416 (4.64), 297 (4.67).

Anal. Calcd. for $C_{21}H_{10}BrN_5O_3S_4$ (major product 4B): C, 42.86%; N, 11.90%; Br, 13.58. Found: C, 43.26%; N, 12.28%; Br, 13.72.

2-(5'-Bromo-7',7',8',8'-tetracyanoquinodimethan-2'-oxy)ethyl tetrathiafulvalenylcarboxylate (5)

A solution of 0.5 mmol of 2-chlorocarbonyltetrathiafulvalene (2c) in 25 mL of CH_2Cl_2 and a solution of 0.027 mL (0.34 mmol) of pyridine in 5 mL of CH_2Cl_2 were added dropwise (separately and simultaneously) to an ice-water cooled and stirred solution of 116 mg (0.34 mmol) of 2-(2'-hydroxyethoxy-5-bromo-7,7,8,8-tetracyanoquinodimethan (3b) in 25 mL of CH_2Cl_2 under an Ar atmosphere during a 30-min period. The resultant mixture was stirred for 12 h at rm. temp. under a slow stream of Ar. Evaporation of the solvent afforded ~0.24 g of a brown-black solid which was triturated with ethanol. The ethanol-insoluble residue (60 mg) was then triturated with CH_3CN. The part of the CH_3CN-insoluble fraction which was soluble in CH_2Cl_2 (12 mg, 6% yield of product 5A) melted at 75-85°C. The thin-layer chromatogram (reverse-phase, 80% CH_3OH: 20% H_2O) showed two zones in close proximity (R_f 0.82).

Anal. Calcd. for $C_{21}H_9BrN_4O_3S_4 \cdot H_2O$: C, 42.64%; H, 1.87%; N, 9.47%; S, 21.68. Found: C, 42.94%; H, 2.10%; N, 7.95%; S, 22.11.

Another sample of a similar fraction from a different run was chromatographed on Sephadex LH-20 (15 $CHCl_3$: 5 heptane: 1 EtOH) to afford a product that was essentially the same as 5A according to TLC: IR (KBr) 3500 (H_2O), 3090, 2940 (CH stretch), 2180 (CN),[7] 1710 (ester carbonyl), 1595, 1525 (quinone), 1230, 1060 cm^{-1} (aryl and alkyl

ethers); UV (CH_3CN) λ_{max}855, 770, 490, 410, 315, 305, and 290 nm, Mass Spectrum (positive fast atom bombardment in thioglycerol matrix): molecular ion isotope cluster at 574-576 (MW 574), and fragment ions at 232 and 342 (TTF and TCNQ portions, respectively).

The ethanol-soluble product from the esterification was concentrated in vacuo to a solid which was washed with water, and then dissolved in CH_2Cl_2; the resultant solution was washed with water. The organic solution was dried and then distilled under reduced pressure to afford a brown solid (50 mg). This was partially purified using droplet countercurrent chromatography (30% $CHCl_3$:40% ethanol:30% H_2O, the lower layer was the mobile phase). The first eleven fractions contained two fast tlc zones whose R_f was almost identical to those described above (isolated from the ethanol-insoluble product). This product (46 mg) was triturated with heptane to yield 36 mg of a granular non-crystalline brown solid (product 5B): mp 110-130° dec.; IR (KBr) 3500 (H_2O), 3090, 2930 (CH stretch), 2210, 2180 (CN),[7] 1725 (ester carboxyl), 1595, 1525 (quinone), 1240, 1060 (aryl and alkyl ethers, respectively); UV (CH_3CN) $\lambda_{max}(\log_{10}\varepsilon)$ 855 nm (2.15), 760 (2.08), 500 (3.18), 460 (3.44), 410 (4.10), 400 (4.10), 300 (3.83).

EXPERIMENTAL: PHYSICAL CHARACTERIZATION

2-(5'-Bromo-7',7',8',8'-tetracyanoquinodimethan-2'-oxy)ethyl phenyl carbamate (7)

The D-σ-A urethane 7 (D = benzene, A = TCNQ) yields small dark crystals which crystallize in space group $P2_1/n$ with unit cell constants a = 831.0(2) pm, b = 927.8(2) pm, c = 2538.3(4) pm, β = 96.15(20)°, Z = 4 for $C_{21}H_{12}BrN_5O_3$. 2229

reflections with $F_{obs} > 2\sigma (F_{obs})$ were collected on an ENRAF-Nonius CAD-4F diffractometer. After a MULTAN-78 trial structure was obtained, it was refined by full matrix least-squares procedures to an agreement index R = 7.9% (271 parameters, 2229 observations). An ORTEP plot of the molecular structure is shown in Fig. 1. The TCNQ ring is quinonoid. The molecular conformation of 7 is extended, there is an 8° angle between the least-squares planes of the phenyl and the TCNQ six-membered rings. The molecules stack D-σ-A atop A-σ-D. Details of this structure will be published elsewhere.[11]

2-(5'-Bromo-7',7',8',8'-tetracyanoquinodimethan-2'-oxy)ethyl tetrathiafulvalenylcarbamate (4)

Preliminary EPR measurements of a powder sample of the major product 4B at 300 K showed an intense broad signal (line width ca. 1 mT) at g ~ 2 with large g-factor anisotropy, no temperature dependence of the intensity was observed in the range 300 K < T .CW 10 <352 K: this suggests that 4B is a ground-state zwitterionic biradical (D^+-σ-A^-). A very concentrated solution of 4A in CH_3CN showed two signals (g = 2.0030, linewidth, 0.45 mT, and g = 2.0080, linewidth 0.3 mT) with different peak heights and no resolved hyperfine structure: these signals in solution could be due to impurities, to biradicals D^+-σ-A (i.e. two decoupled S = 1/2 signals due to TTF^+ and to TCNQ within TTF^+-σ-$TCNQ^-$), or to intermolecular complexes. Since sample purity is a serious problem, the solution EPR data should be viewed with extreme caution. A cyclic voltammogram of 4B shows good reversible oxidation waves, but the reduction waves are not what one would expect. Nevertheless, product 4B seems to be the zwitterionic (D^+-σ-A^-)

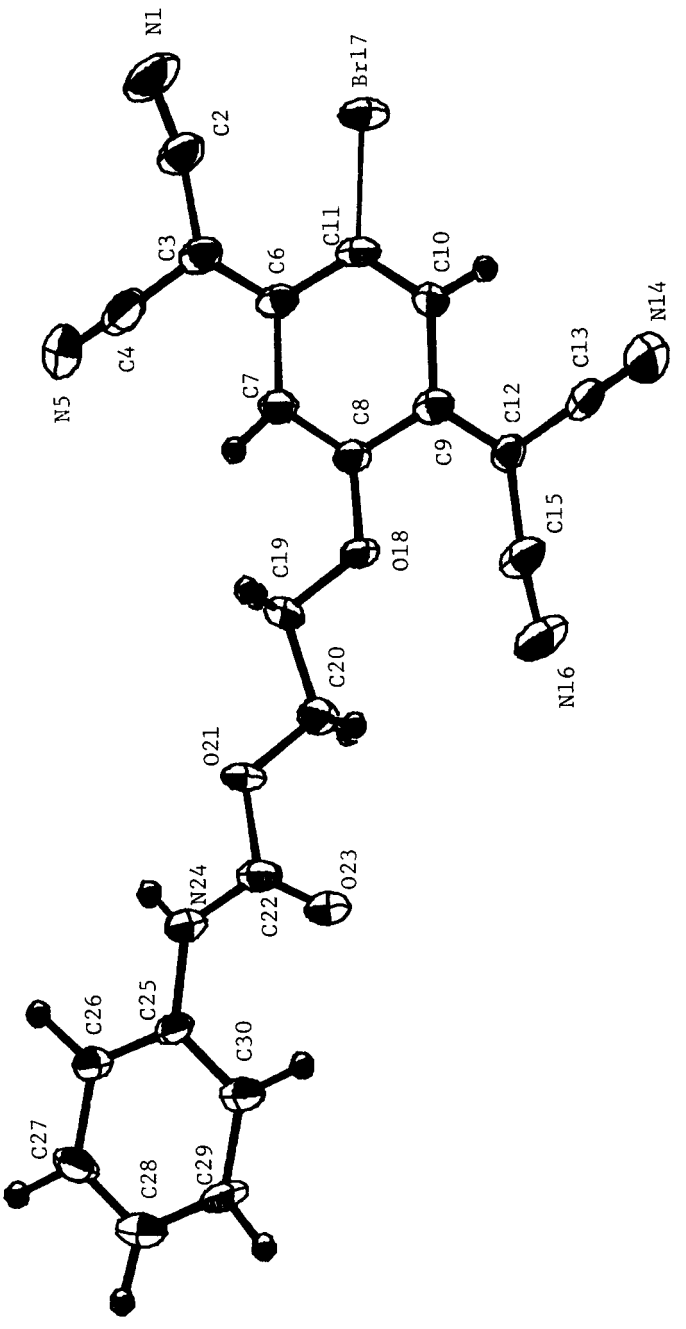

FIGURE 1. ORTEP plot of 2'-(5'-bromo-7',7',8',8'-tetracyanoquinodimethan-2'-oxy) phenyl carbamate (7).

form of 4. In a Lauda film balance[12] 4B dissolves in water, and forms no oriented films.

As reported elsewhere,[5] minor product 4A forms microcrystals [x-ray lines at d = 7.225Å (w^{-5}), 6.981 (w^{-4}), 6.230 (w^{-}), 4.974 (w^{-2}), 4.405 (w^{-5}), 4.282 (w^{-3}), 3.897 (w^{-3}), 3.593 (w^{-4}), 3.515 (w), 3.437 (w^{-5}), 2.926 (w^{-5}), 2.317 (w^{-6}), which can be indexed for five possible triclinic lattices of reasonable cell dimensions]. A Langmuir-Blodgett film has been obtained[12] with product 4A, but electrical rectification was not observed. Details of the experiment are given in Ref. 5.

DISCUSSION

A key feature of the Aviram-Ratner proposal is the easy interconvertibility of D-σ-A and D^{+}-σ-A^{-} states. Therefore it is of some concern that the ground state (neutral or ionic) of the molecules discussed here be firmly established.

The shift of the CN stretching band to a lower frequency (below 2200 cm^{-1}), and its broadening are usually indicative of the radical-anion form of the tetracyanoquinodimethane moiety[7]. Neutral molecules, such as 3b and the phenyl-urethan-TCNQ 7 have sharp peaks at 2210 and 2200 cm^{-1}, respectively. The charge-transfer salt, 3b·Et_3N, and the major products TTF-urethan-TCNQ 4B and TTF ester-TCNQ 5A all have broad CN stretching bands below 2200 cm^{-1}. Thus 4B and 5A seem to be zwitterionic, D^{+}-σ-A^{-}. Much less can be said about minor products 4A (neutral?) and 5B. Sample purification is a serious problem; efforts to obtain crystalline products for 4 and 5 are underway.

In conclusion, Fig. 1 shows that the urethane bond can give a fairly flat and extended geometry, as desired by the Aviram-Ratner proposal, and the preliminary data presented here for molecules 4, 5 support the successful covalent linkage of TTF to TCNQ.

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*Supported by National Science Foundation - Solid State Chemistry - Grant DMR 80-15658

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